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(54) **Modified brass alloys with improved stress relaxation resistance**

(57) The stress relaxation characteristics of alpha-phase brass alloys are improved by the incorporation of 0.05 to 2% tin and

0.05 to 3% silicon into alloys containing 20—34 weight % of zinc. Optionally, grain refining elements such as Fe, Co, Cr, Zr, Mn and/or Ti may be present, as may other elements, such as Pb and As, to improve the machinability and stress corrosion properties of the α -phase brass.

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SPECIFICATION

Modified brass alloys with improved stress relaxation resistance

Material used for spring connection devices must exhibit the ability to maintain adequate contact pressure for the design life of any part formed from the material. This ability to maintain adequate contact pressure is the ability to resist stress relaxation over a period of time, especially at temperatures elevated above normal room temperature. The current trend in connector design has been to place greater emphasis upon the maintenance of high contact pressure on connector parts at mildly elevated temperatures to reduce problems which might develop as the service temperature of the parts increases. Alloy 260 is currently widely used for electrical connectors but tends to exhibit a rather poor stress relaxation resistance at temperatures of 75°C or higher. Accordingly, it is important that this widely used alloy be modified in such a manner so as to improve its elevated temperature stress relaxation performance.

It is important to any modifications of Alloy 260 that high conductivity be maintained along with improved stress relaxation performance. Furthermore, bend formability should be maintained while any cost increase in the alloy should be held down as low as possible to keep such an alloy competitive in the market. Other performance characteristics such as stress corrosion, solderability, softening resistance and others should not be significantly degraded below those properties shown by Commercial Alloy 260. It is desirable to the present invention that the performance of such an alloy exhibit approximately a 10—30% increase over projected stress remaining after 100,000 hours at 75°C or higher relative to Alloy 260. It is also desirable in the present invention that such an alloy maintain approximately a 20% IACS conductivity.

One alloy system which has been developed in the prior art is an improved beta-brass alloy as shown in Patent No. 4,055,445 to Horace Pops. This particular patent teaches a brass alloy which exhibits a shape memory effect and which may contain from 25 to 40% by weight zinc along with 0.25 to 3.0% by weight silicon. It should be noted that the only useful alloy system within this broad range is shown by the cross hatched area in Figure 3 of said patent, wherein the alloy should have a minimum amount of 25% by weight beta-phase up to 75%. Apparently, not only the particular alloy system itself but its specific processing is important in preparing the improved alloy of this particular patent. It is quite important to this patent that an annealing be performed so as to provide the above-mentioned minimum amount of beta-phase material within the alloy system.

In accordance with the present invention it has been discovered that additions of tin or silicon or combinations of tin and silicon to an alpha-brass containing 8 to 34% by weight zinc provide substantial improvements in the stress relaxation behaviour of such an alloy, particularly at large degrees of cold reduction, without appreciably detrimentally affecting the electrical conductivity of the base copper-zinc alloy system. The elemental additions made to the base alloy also provide these increases in performance without appreciably affecting the processing of the alloy system, which contributes to keeping down the cost of such an alloy.

More particularly the present invention provides an alloy system consisting of, apart from impurities, 0.05 to 2.0% by weight tin, 0.05 to 3.0% by weight silicon, the balance of the system being a substantially alpha-base brass containing 20 to 34% by weight zinc. The preferred compositional ranges for these particular additions should range from 0.1 to 2.0% by weight tin and from 0.1 to 2.0% by weight silicon. It should be noted that these additions exhibit an inverse relationship according to the amount of zinc in the alpha-brass base material. In other words, the higher amount of zinc in the base alloy, generally the lower the amount of tin or silicon or silicon plus tin. The optimum compositional range for this alloy system should be from 20 to 32% by weight zinc and 0.1 to 1.5% by weight silicon, 0.1 to 1.0% by weight tin and the balance copper. The most particular compositional range for this alloy is from 26 to 31% by weight zinc, 0.1 to 1.0% by weight silicon, 0.1 to 1.0% by weight tin, provided that the combined silicon plus tin is at least 0.3% by weight, balance copper.

The elemental additions discussed above maintain an essentially single-phase alpha alloy. It should be stressed that beta-phase formation should be avoided as much as possible. Although immediately after casting and solidification non-equilibrium beta-phase may be present within the alloy system, further processing of the alloy should try to keep the beta-phase to a maximum of 10 wt. percent. In particular, the alloy system of the present invention should not be annealed in an alpha plus beta or a beta-phase region. The presence of the beta-phase adversely affects the cold workability of the alloy as well as its stress corrosion resistance. Various other elements may be added to the alloy of the present invention to suit various purposes. For example, a grain refining element selected from the group consisting of 0.001 to 5.0% by weight iron, 0.001 to 5.0% by weight cobalt, 0.001 to 1.0% by weight chromium, 0.001 to 1.0% by weight zirconium, 0.001 to 1.0% by weight nickel, 0.001 to 1.0% by weight titanium, or any combination thereof may be added to the alloy. Various other elements such as lead may be added to improve the machinability of the alloy and elements such as arsenic may be added to improve the stress corrosion performance of the alloy. Naturally, the alloy of the present invention may also contain impurities common for alloys of this type and additional additives may be employed in the alloy, as desired, in order to emphasize particular characteristics or to obtain particularly desirable results. The inclusion of such additives in the amounts and for the purposes

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specified is to be embraced within the term 'brass'.

It has normally been expected in this art that an increase in the yield strength of such an alloy should provide an improvement in the stress relaxation performance of the alloy. The improvements brought about by the alloy system of the present invention are considerably greater than those improvements which can be realized by increasing the yield stress alone. These modifications made in the present invention do raise the yield strength of Alloy 260 brass by as much as 13% while they raise the stress remaining values of the alloy by as much as 30%. It is this unexpected increase in the stress remaining value of the alloy system which provides the surprising benefits of the present invention.

The processing of the alloys of the present invention includes various stages of hot and cold working along with various annealing stages. The hot working of this alloy system should be done at a minimum temperature which is above the recrystallization temperature of the particular alloy being worked and which is below the solidus temperature of the alloy. This temperature will range between 500 and 1000°C or preferably between 600 and 900°C. An optional step after hot working in the processing can be a diffusion annealing step. This annealing will utilize a temperature range of from 200 to 800°C for 1 to 24 hours or preferably a range of 400 to 700°C for 1 to 12 hours. The alloy can then be subjected to a milling step, whether or not it undergoes the annealing step, in order to clean the surface of the worked alloy and prepare it for further working. The alloy may then be cold worked with up to but not including a 100% reduction in area and preferably a 10 to 98% reduction in cross-sectional area. The cold worked material can then be subjected to an annealing step at 150 to 900°C for enough time to recrystallize the alloy to a grain size of 0.005 to 0.05 mm. This annealing can be accomplished in cycles with cold working steps provided that cold working is that last step of the cycle. Cleaning of the worked material can be performed after any one of the annealing steps and not necessarily after each annealing step.

The present invention will be more readily understood from a consideration of the following illustrative examples.

EXAMPLE I

Alloys of the present invention were all made by adding the elemental additions to molten copper at approximately 1100°C. The zinc was added at approximately 1050°C and all ingots were poured at 950 to 1050°C. These ingots were then soaked at 800°C for 2 hours prior to hot working by rolling down to a 0.48" gage and then both rolled surfaces were milled to a final gage of 0.4". Subsequent processing consisted of cold working up to a 90% reduction with interanneals of 550°C for one hour in air between each cold working pass. The material utilized in this processing was given a final anneal such that the grain size of the alloy was approximately 0.010 mm.

Various alloys were cast in air as 10 lb. ingots with the compositions in weight percent as shown in Table I. Four control alloys of copper-30% zinc were cast and the average properties of the four controls were utilized at subsequent measurements. An additional alloy of commercially processed copper-30% zinc brass was also utilized. The appropriate amounts of the required elements were added to molten copper and the melts were poured through a tundish into a chilled mold. The processing of the alloys consisted of soaking at 800°C for 2 hours followed by hot rolling to 0.48" and surface milling down to 0.4". The alloys were subsequently cold rolled with intermediate annealing. This annealing was utilized to provide a grain size in the alloy prior to a final cold reduction of 0.01 mm. The final cold rolling reductions were either 35% or 60%, which values were selected for property measurement at each point.

Samples were machined from the 0.03" final gage material after cold working and were tested for their stress relaxation behavior in the longitudinal direction at 75°C. Initial loading was set at 80% of the 0.2% offset yield stress for each alloy. Data for percent stress remaining at 1,000 or more hours of testing were extrapolated to 100,000 hours. The logarithm of stress remaining versus the logarithm of time and hours was assumed to be a linear relationship. The results are presented in Table II.

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TABLE I
NOMINAL COMPOSITIONS OF ALLOYS

Alloy No.	% Zn	Composition		% Cu
		% Si	% Sn	
Control	30	—	—	Rem.
Commercial Alloy 260	30	—	—	Rem.
C247	27	0.4	—	Rem.
A948	30	—	0.5	Rem.
C248	27	0.4	0.5	Rem.
C311	27	0.3	0.4	Rem.
C312	27	0.4	0.3	Rem.
C313	27	0.5	0.2	Rem.
C314	27	0.6	0.1	Rem.

TABLE II
ALLOY PROPERTIES

Alloy	% CW	0.2% YS	UTS	% Elong.	MBR (In 1/64")*	Initial Stress	Stress Relaxation Behaviour		
							Actual 1,000 H. % Stress Remaining	Extrapolated 100,000 H. % Stress Remaining	Extrapolated 100,000 H. Stress Remaining
Control	35 60	71.4 86.1	79.7 99.6	7.7 2.8	4 16	57.1 68.9	76.8 70.4	66.9 59.4	38.2 40.9
Commercial Alloy 260	60	85.8	102.0	2.5	N.A.	68.6	68.1	56.9	39.0
C311	35 60	81.9 95.4	90.3 108.1	6.1 2.9	5 16	65.5 76.3	82.0 75.2	75.1 65.0	49.2 49.6
C312	35 60	81.8 93.1	91.2 107.0	6.8 2.4	4 16	65.4 74.5	82.7 77.0	76.6 66.9	50.1 49.8
C313	35 60	83.2 98.9	92.8 108.1	7.5 2.8	4 16	66.6 79.1	85.2 75.9	79.6 65.9	53.0 52.1
C314	35 60	83.3 96.1	93.5 108.6	6.7 2.8	4 16	66.6 76.9	83.4 76.3	77.0 66.7	51.3 51.3
C248	35 60	80.9 93.2	91.5 109.5	6.0 1.0**	4 20	64.7 74.6	84.4 77.3	79.0 69.3	51.1 51.7

* In Transverse Direction.

** Broke outside gage marks.

N.A. — Not Available.

YS, UTS, Initial Stress and Stress Remaining Values are all in ksi.

As can be seen from Table II, the alloys according to the present invention exhibit surprising stress relaxation resistance behavior when compared to either Commercial Alloy 260 or a similar laboratory manufactured material. The Stress Remaining portion of Table II extrapolated to 100,000 hours indicates that the benefits derived from the present invention are more than can be expected from a simple increase in yield strength compared to the base alloys. For example, while the yield strength of Alloy C313 the composition of which falls within the present invention, is only 9.8 ksi and 10.2 ksi at 35% cold worked and 60% cold worked greater than the Control Alloy, the Stress Remaining at 100,000 Hours is 14.8 and 11.2 ksi greater at these cold working reductions than the Control Alloy. This clearly demonstrates the unexpected and surprising improvement in stress relaxation resistance brought about by the alloys of the present invention.

EXAMPLE II

The alloys listed in Table I were processed as described in Example I and the Stress Remaining after 100,000 Hours was determined based on Initial Stress levels of 60 and 70 ksi corresponding to hard temper brass and spring temper brass, respectively. The percentage difference over the average Cu-30% Zn base alloy was also measured. The results are shown in Table III.

Electrical conductivities for each of these alloys were measured in various degrees of worked and annealed conditions. These results are shown in Table IV.

TABLE III
STRESS REMAINING AFTER 100,000 HOURS AND IMPROVEMENT OVER BRASS CONTROLS BASED ON
INITIAL STRESS LEVELS OF 60 AND 70 KSI

Alloy No.	Nominal Composition	60 ksi Initial Stress			70 ksi Initial Stress		
		% SR	100,000 H. SR	% Difference Over Average Cu-30 Zn	% SR	100,000 H. SR	% Difference Over Average Cu-30 Zn
Average of Cu-30 Zn Controls	Cu-30 Zn	65.4	39.2	-	60.0	42.0	-
C247	Cu-27 Zn-0.4 Si	77.3	46.4	+18	67.0	46.9	+12
A948	Cu-30 Zn-0.5 Sn	75.1	45.0	+15	66.7	46.7	+11
C248	Cu-27 Zn-0.4 Si-0.5 Sn	83.6	50.2	+28	73.8	51.7	+23
C311	Cu-27 Zn-0.3 Si-0.4 Sn	80.2	48.1	+23	70.9	49.6	+18
C312	Cu-27 Zn-0.4 Si-0.3 Sn	82.4	49.4	+26	71.7	50.2	+20
C313	Cu-27 Zn-0.5 Si-0.2 Sn	86.8	52.1	+33	75.9	53.1	+27
C314	Cu-27 Zn-0.6 Si-0.1 Sn	83.6	50.2	+28	73.6	51.5	+23

TABLE IV
CONDUCTIVITY PROPERTIES*

Alloy No.	Condition	Conductivity (% IACS)
Control	35% CW	26.0
C248	Annealed	21.1
C311	60% CW	20.5
C312	Annealed	21.7
C313	60% CW	18.5
C314	Annealed	19.4

*Values for conductivity in the cold worked condition are typically 1.5 to 2.5% IACS lower than the annealed values.

It can be readily be seen from Table III that the silicon and tin additions to the copper-zinc base provide significant improvements in the stress remaining values over the average of the copper-30 zinc controls. It is quite apparent from Table III that the improvements brought about by the silicon and tin additions appear to be concentration dependent in that the percentage difference over the average control values increases as the percentage of silicon and tin increases in the base alloy. The improvement brought about by the combination of silicon and tin appears to be a result of a synergistic combination of these two elements since it would be expected from the alloys with silicon or tin alone that a lower amount of improvement would result from a combination of these elements. For example, Alloy C247 at 60 ksi initial stress exhibits an 18% improvement over the control alloy values. Alloy A948 exhibits a 15% improvement at the same initial stress value. Alloy C248, which contains a mixture of the same amounts of silicon and tin found in Alloys C247 and A948, respectively, exhibits a 28% improvement over the control values at the same initial stress. It would not be expected that simply adding these two elements together in a copper-zinc base would provide such a large improvement.

It should be noted from Table IV that in most instances the addition of a mixture of silicon plus tin to a copper-zinc base reduces the electrical conductivity somewhat when compared to the control material. There appears to be a trade off point between desired conductivity and desired resistance to stress relaxation. The large percentage improvements demonstrated by the silicon plus tin additions to the base alloy in Table III offset somewhat the relatively small decrease in conductivity exhibited by these same alloys in Table IV.

CLAIMS

1. A hot workable, stress relaxation resistant alloy consisting of a substantially single phase alpha brass alloy containing from 20—34% by weight of zinc, to which has been added 0.05 to 2.0% by weight tin and 0.05 to 3.0% by weight silicon, provided that the combined silicon plus tin content of the alloy is at least 0.3% by weight.
2. An alloy according to claim 1 characterised in that said tin is from 0.1 to 2.0% by weight and said silicon is from 0.1 to 2.0% by weight.
3. An alloy according to claim 1 characterised in that said tin is from 0.1 to 1.0% by weight, said silicon is from 0.1 to 1.5% by weight and said zinc is from 20 to 32% by weight.
4. An alloy according to claim 1 characterised in that said tin and silicon are from 0.1 to 1.0% by weight each and said zinc is from 26 to 31% by weight.
5. An alloy according to any one of the preceding claims characterised in that said alloy is in the worked condition and has a grain size of approximately 0.005 to 0.050 mm.
6. A method for producing a hot workable stress relaxation resistant brass alloy which comprises
 - (a) casting a brass alloy having a zinc content of 20—34% and containing from 0.05 to 2.0% by weight tin and 0.05 to 3.0% by weight silicon in total amount of at least 0.3% by weight;
 - (b) hot working said alloy at a temperature above the recrystallization temperature of the alloy and below the solidus temperature of the alloy;

(c) cold working said alloy with up to but not including a 100% reduction in area; and
 (d) annealing the worked alloy at 150 to 900°C to recrystallize the alloy to a grain size of 0.005 to 0.050 mm.

7. A method according to claim 6, characterised in that said cold working is accomplished in
 5 cycles with said annealing, provided that a cold working step is the last step of the cycle. 5
 8. A method according to claim 6 or 7, characterised in that said alloy is annealed at 200 to
 800°C for 1 to 24 hours after said hot working but before said cold working.
 9. A method according to claim 6, 7 or 8, characterised in that said hot working is at 500 to
 1000°C.
 10. A method according to any one of claims 6 to 9, characterised in that said cold working
 10 utilises a 10 to 98% reduction in cross-sectional area of said alloy.
 11. A method according to any one of claims 6 to 10, characterised in that the cast brass alloy
 contains: 20 to 32% by weight zinc, 0.1 to 1.0% by weight tin and 0.1 to 1.5% by weight silicon.

CLAIMS

1. A hot workable, stress relaxation resistant alloy consisting of a substantially single phase alpha
 15 brass alloy containing from 20—34% by weight of zinc, to which has been added 0.1 to 2.0% by weight
 tin and 0.1 to 2.0% by weight silicon provided that the combined silicon plus tin content of the alloy is
 at least 0.3% by weight. 15
 2. An alloy according to claim 1 characterised in that said tin is from 0.1 to 1.0% by weight, said
 20 silicon is from 0.1 to 1.5% by weight and said zinc is from 20 to 32% by weight. 20
 3. An alloy according to claim 1 characterised in that said tin and silicon are from 0.1 to 1.0% by
 weight each and said zinc is from 26 to 31% by weight.
 4. An alloy according to any one of the preceding claims characterised in that said alloy is in the
 worked condition and has a grain size of approximately 0.005 to 0.050 mm.
 25 5. A method for producing a hot workable stress relaxation resistant brass alloy which comprises 25
 (a) casting a brass alloy having a zinc content of 20—34% and containing from 0.1 to 2.0% by
 weight tin and 0.1 to 2.0 by weight silicon in total amount of at least 0.3% by weight;
 (b) hot working said alloy at a temperature above the recrystallization temperature of the alloy and
 below the solidus temperature of the alloy;
 30 (c) cold working said alloy with up to but not including a 100% reduction in area; and 30
 (d) annealing the worked alloy at 150 to 900°C to recrystallize the alloy to a grain size of 0.005 to
 0.050 mm.
 6. A method according to claim 5, characterized in that said cold working is accomplished in
 cycles with said annealing, provided that a cold working step is the last step of the cycle.
 35 7. A method according to claim 5 or 6, characterised in that said alloy is annealed at 200 to 35
 800°C for 1 to 24 hours after said hot working but before said cold working.
 8. A method according to claim 5, 6 or 7, characterised in that said hot working is at 500 to
 1000°C.
 9. A method according to any one of claims 5 to 8, characterised in that said cold working utilises
 40 a 10 to 98% reduction in cross-sectional area of said alloy. 40
 10. A method according to any one of claims 5 to 9, characterised in that the cast brass alloy
 contains: 20 to 32% by weight zinc, 0.1 to 1.0% by weight tin and 0.1 to 1.5% by weight silicon.

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